Reaction of *cis*-2,3-Dioctylaziridine with Carboxylic Acids

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A series of aliphatic and aromatic carboxylic acids reacted with 2,3-dioctylaziridine to yield β-hydroxyalkyl amides in 69-89% yields and 2-substituted 4,5-di-*n*-octyl-Δ^2-oxazolines in amounts ranging from traces to 12% of the theoretical. No correlation could be found between carboxylic acid strength and either hydroxyamide or Δ^2-oxazoline yields. Solvents affected the product distribution.
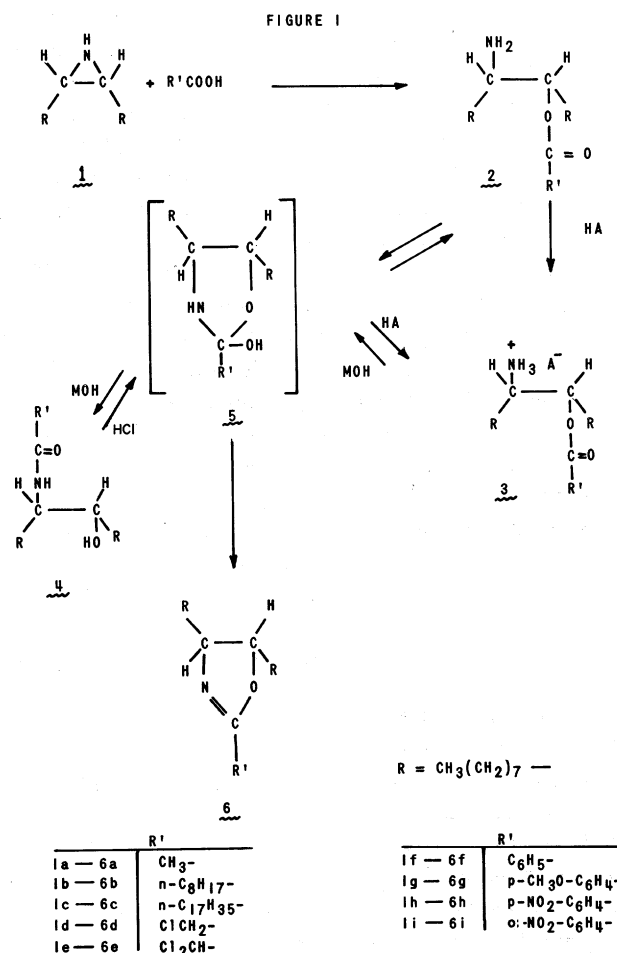
Introduction

Through recent improvements in methods of synthesis of 2,3-dialkylethyleneimines (2-4) long-chain aliphatic internal aziridines have become readily accessible. Our interest in the chemistry of such compounds led us to an investigation of the reaction of these small-ring nitrogen compounds with carboxylic acids. A preliminary communication regarding this work has appeared (5).

The addition of acetic acid to aziridines derived from low molecular weight aliphatic olefins, or from alicyclic olefins, is known to result in *trans* addition with rupture of a carbon-nitrogen bond (6-8). The products have been described variously as β-aminoesters or as the isomeric β-hydroxyamides. Powers *et al.*, (9,10) established that benzoic acid adds to terminal aziridines to give the β-aminoesters, isolable as salts, which rearrange to the isomeric β-hydroxyamides in neutral or alkaline media. Substituted benzoic acids behave similarly. The addition of acetate and of other nucleophiles to substituted terminal aziridines has been studied kinetically by Clapp *et al.*, (11) with regard to mechanism. Johnson and coworkers (12) investigated the reaction of acetic acid with tris-(2-methylaziridinyl) phosphine oxide, and Heine *et al.*, demonstrated (13) that certain N-substituted 2,3-diaroylethyleneimines form unsaturated secondary amines on contact with acetic acid. Recently, McGhie and Warren (14) reported that certain aliphatic *cis*- and *trans*-aziridinylalkan-1-ols are attacked by acetic acid to give *threo*- and *erythro*-aminodiols, respectively, which were characterized as their N-acetyl derivatives.

The present work was undertaken to study the reaction of various aliphatic and aromatic carboxylic acids with *cis*-2,3-dioctylaziridine. The latter compound was chosen as a model for long-chain aliphatic internal aziridines in general, since its symmetry and its lack of interfering functional groups were expected to simplify product isolation and identification. The anticipated course of the reaction is shown in Figure 1. The initial product **2**, the β-aminoester, is expected to be formed as the result of initial protonation of the heterocyclic nitrogen atom followed by nucleophilic attack at one of the carbon atoms of the three-membered ring. In neutral or alkaline medium such esters of β-amino alcohols are known (10) to rearrange to the isomeric β-hydroxyamides (**4**). It was hoped

FIGURE I

$R = CH_3(CH_2)_7 -$

	R'			R'
1a — 6a	CH_3-		1f — 6f	C_6H_5-
1b — 6b	$n-C_8H_{17}-$		1g — 6g	$p-CH_3O-C_6H_4-$
1c — 6c	$n-C_{17}H_{35}-$		1h — 6h	$p-NO_2-C_6H_4-$
1d — 6d	$ClCH_2-$		1i — 6i	$o-NO_2-C_6H_4-$
1e — 6e	Cl_2CH-			

that a carboxylic acid (R'-COOH) of sufficient acid strength would stabilize the β-aminoester (2) and permit isolation of the carboxylate salt (3), just as the hydrochloride of 2 can be formed and isolated. This hope, however, was not realized.

Results and Discussion

The present work demonstrates that the principal isolable products resulting from the reaction of carboxylic acids with cis-2,3-dioctylaziridine are hydroxamides, rather than amino esters, and that Δ^2-oxazolines are also formed. Assignment of the hydroxyamide (4) structures is based upon the following evidence: (a) elemental analyses agree with the calculated values; (b) the compounds have characteristic infrared bands at 3400-3440 cm^{-1} (-OH), 3310-3340 cm^{-1}(N-H stretch), 1620-1635 cm^{-1} and 1535-1550 cm^{-1} (amide), while ester bands are absent; (c) the compound formed from 2,3-dioctylaziridine and acetic acid resists hydrolysis by refluxing methanolic potassium hydroxide, is acylated by acetic anhydride-pyridine to form an ester-amide which can be hydrolyzed by methanolic potassium hydroxide to reform the starting material; (d) treatment of the pure material (formed from 2,3-dioctylaziridine and benzoic acid) in dioxane with anhydrous hydrogen chloride gives rise to a new compound in which all of the characteristic hydroxyamide IR bands are absent, and new bands at 1725 cm^{-1} (ester) and at 2600-3100 cm^{-1} (amine salt) have appeared. Treatment of the latter product with weak base results in reconversion to the hydroxyamide.

Characterization of the by-products as Δ^2-oxazolines was established in two cases [2-phenyl- and 2-(4-nitrophenyl)-4,5-dioctyl-Δ^2-oxazoline] by comparison of analytical data (IR, TLC, GLC) with those of compounds prepared by the thermal dehydration of the corresponding hydroxyamides. The latter Δ^2-oxazolines gave elemental analyses and mass spectra compatible with the assigned structures.

The amounts in which hydroxyamides and oxazolines are obtained depend upon the carboxylic acid used, the solvent, and the work-up conditions. One set of comparative yields was obtained by allowing 2,3-dioctylaziridine in acetone to react with several different carboxylic acids, and working up the reaction products in identical fashion. Final product isolation was accomplished by adsorption chromatography on Florisil (see Experimental Section). Reactions were carried out for a sufficient period of time to insure complete reaction of the aziridine, as judged by TLC methods capable of detecting at least 1% of 2,3-dioctylaziridine. The data (listed in Table I) indicate that hydroxy amide yields are in the 69-89% range while oxazoline amounts vary from traces to about 12%. In general, the aliphatic acids seem to give slightly greater amounts of hydroxyamide and definitely lower amounts of oxazolines than the aromatic acids, but there is no obvious correlation between acid strength and either hydroxyamide or oxazoline yields in this system. Furthermore, the relative isolated amounts of the two products may not be strictly representative of the amounts formed. Presently continuing stability studies indicate that 2-alkyl-Δ^2-oxazolines are hydrolyzed much more readily to the hydroxy amides than the corresponding 2-aryl-Δ^2-oxazolines. Low yields of oxazolines isolated from the reaction of aliphatic acids with 2,3-dioctylaziridine may then in part reflect the instability of these oxazolines toward work-up conditions.

In view of these considerations it would be desirable to determine the oxazoline content of the crude reaction products, but no reliable procedure has been found to accomplish this. Pure oxazolines can be determined quantitatively in glacial acetic acid solution by titration with a solution of standard perchloric acid in acetic acid against crystal violet indicator. This method, however, is inapplicable to the crude products which contain impurities arising from side reactions of 11-25% of the initial aziridine. These impurities are highly polar, basic materials which interfere with the titrimetric determination of both the residual aziridine and the oxazoline formed. Extraction methods were unsuccessful in separating these impurities, and adsorption chromatography was the only method found to give reasonable reproducible results. Even in this latter procedure, however, caution was required, since prolonged contact of oxazolines with moist air, or briefer exposure to moisture in the presence of chromatographic adsorbent, caused partial hydration to hydroxyamides.

Exploratory experiments indicate that both the hydroxyamide-oxazoline ratio and the amount of polar byproduct can be affected by modification of the reaction solvent. For instance, in aqueous acetone (30% water) p-nitrobenzoic acid gave 84.4% hydroxyamide (15.5% more than in anhydrous acetone), 10.1% oxazoline and 5% polar byproducts (almost 20% in anhydrous acetone).

Furthermore in methanol benzoic acid yielded 39.7% hydroxyamide, 30.3% oxazoline and 30% of unidentified byproducts while the corresponding yields in acetone were 71.6%, 12.3% and 16.1%, respectively. The influence of solvent is being investigated further in this laboratory.

For terminal aziridines it has been clearly established (8-10) that reaction with carboxylic acids occurs by protonation of the heterocyclic nitrogen atom and nucleophilic attack at one of the carbon atoms of the three-membered ring. The resulting carboxylic acid salt of the aminoester has been isolated and characterized. All of our attempts to isolate similar aminoester derivatives of 2,3-

dioctylaziridine were unsuccessful. However, the intermediacy of the aminoester can be inferred from the following information relating to oxazoline formation:

Oxazolines are *bona fide* byproducts rather than secondary products resulting from dehydration of hydroxy amides. This must be so since pure hydroxamide **4h** showed no evidence of oxazoline formation when exposed to the original reaction medium or to the various work-up procedures. On the other hand, a significant amount of oxazoline **6h** was obtained when pure **4h** was first converted to the hydrochloride of **2h** by means of anhydrous hydrogen chloride (15) and the hydroxamide was then reconstituted by treatment with base. It seems quite likely, then, that most, if not all of the oxazoline observed as reaction product, is formed during the acyl migration, and that the aminoester is therefore established as the likely precursor for the oxazoline as well as for the hydroxyamide. This acyl migration proceeds *via* the cyclic intermediate first proposed by Welsh (16) and confirmed by van Tamelen (14).

TABLE I

Reaction of 2,3-Dioctylaziridine with Carboxylic Acids (1)

Carboxylic Acid		Reaction Time	Yield (2) (%)	
Acid	Ka x 10^{-5}	(hr)	Hydroxyamide	Oxazoline
Acetic	1.75	22	77.0	2.0
Pelargonic	1.11	22	88.7	<1.0
Stearic	)	22	79.5	<1.0
Chloroacetic	155	18	74.6	<1.0
Dichloroacetic	5000	6	81.1	2.9
Benzoic	6.35	4	71.6	12.3
Anisic	3.38	19	73.2	7.4
p-Nitrobenzoic	37.6	23	68.9	11.7
o-Nitrobenzoic	671	18	76.5	7.8

(1) Solvent: Acetone, 4 ml. per g. of aziridine. Molar ratio of acid to aziridine = 1.25:1.   (2) Yields of chromatographed product.

EXPERIMENTAL

Material

Carboxylic Acids.

All carboxylic acids were reagent grade or laboratory purified materials. GLC and TLC analysis of their methyl esters indicated a purity of 95% or greater.

cis-9-Octadecane.

cis-9-Octadecenol was converted to the tosylate and the latter reduced with lithium aluminum hydride (17). The crude product was distilled, and the heart cut collected. The product, b.p. 110-112° at 0.25 mm Hg, n$_D^{30}$ = 1.4428 [lit. n$_D^{25}$ = 1.4450 (18)] was examined by GLC using a 2 ft x ¼ in column of 3% OV17 on 100 mesh Chromosorb W and was found to be essentially pure C$_{18}$ olefin. Complete absence of the 968 cm^{-1} band in the infrared spectrum indicated that *trans*-9-octadecene was absent.

2,3-Dioctylaziridine.

cis-9-Octadecene was converted to its aziridinyl derivative by the iodine isocyanate method of Gebelein *et al.*, (4). The product, m.p. 64.5-65.0° [lit. 65-66° (4)] was 98.9% pure by titration with hydrogen iodide formed *in situ* from tetra-*n*-butyl ammonium iodide and standard perchloric acid (19,20).

Procedures.

Preparation of Hydroxamides. Method A.

9-Acetamido-10-hydroxyoctadecane (**4a**).

A solution of 2,3-dioctylaziridine (5.0 g. 0.0187 mole) in 50 ml. of glacial acetic acid was heated at reflux for 2 hours and was then evaporated on the steam bath under a stream of nitrogen. The residue was dissolved in ether (200 ml.), washed with water (2 x 25 ml.), dried over Drierite, filtered, and evaporated to a white, waxy solid (5.48 g.). The latter was recrystallized three times from acetone to obtain a white, crystalline solid, m.p. 88.2-88.7°; I.R. (neat) 3450 (OH), 3350 (NH), 1640 (C=O), 1550 (Amide II), 1460, 1360, 1120 and 1075 cm^{-1}. TLC, developed with a mixture of benzene (90 parts), ether (10 parts) and methanol (3 parts) gave a single spot.

Anal. Calcd. for C$_{20}$H$_{41}$NO$_2$: C, 73.33; H, 12.62; N, 4.28; OH, 5.19. Found: C, 73.34; H, 12.55; N, 4.48, OH, 5.10.

9-Nonanoamido-10-hydroxyoctadecane (**4b**).

2,3-Dioctylaziridine (1.0 g., 0.00374 mole) and nonanoic acid (5.0 g., 0.0312 mole) were heated with stirring at 67-69° for 6.5 hours and allowed to cool. Recrystallization from methyl acetate gave white crystals, m.p. 73.0-73.5°; I.R. (neat) 3425 (OH), 3325 (NH), 1640 (C=O) and 1540 (Amide II), cm^{-1}.

Anal. Calcd. for C$_{27}$H$_{55}$NO$_2$: C, 76.17; H, 13.02; N, 3.29; OH, 3.99. Found: C, 76.26; H, 12.98; N, 3.24; OH, 4.32.

9-Stearamido-10-hydroxyoctadecane (**4c**).

2,3-Dioctylaziridine (1.0 g., 0.00374 mole) and stearic acid (8.4 g., 0.0295 mole) were mixed and heated with stirring at 82-83° for 5 hours. After removal of the excess stearic acid, the product was recrystallized from acetone to give white crystals with m.p. 69.3-70.0°; I.R. (neat) 3425 (OH), 3300 (NH), 1640 (C=O) and 1540 (Amide II) cm^{-1}.

Anal. Calcd. for C$_{36}$H$_{73}$NO$_2$: C, 78.32; H, 13.33; N, 2.54; OH, 3.08. Found: C, 78.85; H, 13.38; N, 2.58; OH, 2.96.

Method B.

9-Benzamido-10-hydroxyoctadecane (**4f**).

A solution of 2,3-dioctylarizidine (1.0 g., 0.00374 mole) and benzoic acid (4.58 g., 0.0374 mole) in acetone (10 ml.) was heated at reflux for 2 hours. The mixture was diluted with 45 ml. of acetone and the solution cooled at -20°. The solids were filtered, dried (0.81 g.) and recrystallized from acetone (6.5 ml.) at room temperature to obtain white crystals (0.67 g., m.p. 86.2-86.9°), an analytical sample was recrystallized twice more from acetone yielding white crystals, m.p. 86.0-86.5°; I.R. (neat) 3425 (OH), 3300 (NH), 1625 (C=O), 1600, 1575, 1525 (Amide II), 1075, 725 and 680 cm^{-1}.

Anal. Calcd. for $C_{25}H_{43}NO_2$: C, 77.07; H, 11.12; N, 3.60; OH, 4.37. Found: C, 76.86; H, 11.06; N, 3.75; OH, 4.22.

9-(4-Methoxybenzamido)-10-hydroxyoctadecane (4g).

A solution of 2,3-dioctylaziridine (1.0 g., 0.00374 mole) and *p*-methoxybenzoic (anisic) acid (5.69 g., 0.0374 mole) in acetone (55 ml.) was heated at reflux for 2 hours. The crude product was crystallized from acetone to give white crystals, m.p. 106.5-107.0°, I.R. (neat) 3425 (OH), 3350 (NH), 1610 (C=O), 1540 (Amide II), 1505, 1250, 1025, 840 and 760 cm^{-1}.

Anal. Calcd. for $C_{26}H_{45}NO_3$: C, 74.41; H, 10.81; N, 3.34; OH, 4.05. Found: C, 74.85; H, 10.84; N, 3.40; OH, 4.07.

9-(4-Nitrobenzamido)-10-hydroxyoctadecane (4h).

A solution of 2,3-dioctylaziridine (1.0 g., 0.00374 mole) and *p*-nitrobenzoic acid (0.77 g., 0.00461 mole) in acetone (4 ml.) was heated at reflux for 23 hours. The pure product was obtained by crystallization from acetone as pale yellow crystals with m.p. 90-91°; I.R. (neat) 3400 (OH), 3320 (NH), 1640 (C=O), 1590, 1530 (Amide II), 1540 and 1340 (NO$_2$), 870 and 725 cm^{-1}.

Anal. Calcd. for $C_{25}H_{42}N_2O_4$: C, 69.09; H, 9.74; N, 6.45. Found: C, 69.2; H, 9.47; N, 6.83.

9-(2-Nitrobenzamido)-10-hydroxyoctadecane (4i).

A solution of 2,3-dioctylaziridine (1.0 g., 0.00374 mole) and *o*-nitrobenzoic acid (0.78 g., 0.00468 mole) in 4 ml. of acetone was heated at reflux for 2 hours. Recrystallization from acetone gave pale yellow crystals, m.p. 85-85.5°; I.R. (neat) 3400 (OH), 3280 (NH), 1640 (C=O), 1540 (Amide II), 1525 and 1350 (NO$_2$), 1075, 850 and 775 cm^{-1}.

Anal. Calcd. for $C_{25}H_{42}N_2O_4$: C, 69.09; H, 9.74; N, 6.74. Found: C, 68.85; H, 9.62; N, 6.70.

9-Chloroacetamido-10-hydroxyoctadecane (4d).

2,3-Dioctylaziridine (1.0 g., 0.00374 mole) and chloroacetic acid (0.44 g., 0.00468 mole) were dissolved in 4 ml. of acetone and the solution heated at reflux for 2 hours. Crystallization from 10 parts acetone gave white crystals, m.p. 76.5-77°; I.R. (neat) 3425 (OH), 3315 (NH), 1640 (C=O), 1550 (Amide II), 1470, 1410, 1260, 1075, 775 and 720 cm^{-1}.

Anal. Calcd. for $C_{20}H_{40}ClNO_2$: C, 66.36; H, 11.14; N, 3.87; Cl, 9.79. Found: C, 66.14; H, 11.07; N, 3.69; Cl, 10.10.

9-Dichloroacetamido-10-hydroxyoctadecane (4c).

2,3-Dioctylaziridine (1.0 g., 0.00374 mole), dichloroacetic acid (0.60 g., 0.00468 mole) and 4 ml. of acetone were combined and heated at reflux for 2 hours. Crystallization from acetone gave the pure compound as white crystals with m.p. 78.0-78.5°; I.R. (neat) 3460 (OH), 3320 (NH), 1660 (C=O), 1550 (Amide II), 1400, 1125, 1075 and 720 cm^{-1}.

Anal. Calcd. for $C_{20}H_{39}Cl_2NO_2$: C, 60.59; H, 9.92; N, 3.53; Cl, 17.89. Found: C, 60.73; H, 9.94; N, 3.42; Cl, 17.86.

Preparation of Δ^2-Oxazolines.

4,5-Di-*n*-octyl-2-phenyl-Δ^2-oxazoline (6f).

9-Benzamido-10-hydroxyoctadecane, 4f (2.0 g., 0.00513 mole) was heated at 195-205° under a stream of nitrogen for 2 hours. The cooled product, dissolved in hexane, was placed on a column of silica gel (60 g.) packed in hexane. Elution with benzene-hexane (1:1) gave a clear, colorless oil (1.42 g., n_D^{27} = 1.4943) yield 74.3%; I.R. (neat) 2940, 1650 (C=N), 1490, 1450, 1075, 1055, 1020 and 690 cm^{-1}.

Anal. Calcd. for $C_{25}H_{41}NO$: C, 80.80; H, 11.12; N, 3.77. Found: C, 80.88; H, 10.85; N, 3.90.

4,5-Di-*n*-octyl-2-(4-nitrophenyl)-Δ^2-oxazoline (6h).

(a) From 2,3-Dioctylaziridine.

2,3-Dioctylaziridine (5.0 g., 0.0187 mole), *p*-nitrobenzoic acid (31.25 g., 0.187 mole) and acetone (350 ml.) were heated at reflux for 2.75 hours. The product mixture was cooled and evaporated *in vacuo* to a solid residue. The latter, dissolved in chloroform (750 ml.), was washed with 5% aqueous sodium hydroxide until the aqueous washes gave no precipitate on acidification. The organic solution was washed with water, dried over magnesium sulfate, and evaporated to a solid residue (7.25 g.). The latter, dissolved in acetone (57 ml.), was cooled at -15°, the crystalline solid (crude hydroxyamide) removed by filtration, and the filtrate evaporated *in vacuo* to 13 ml. volume. Cooling at -15° and filtration gave a second crop of crystals. The filtrate was evaporated to a residual oil (2.3 g.). A portion of this oil (2.0 g.) dissolved in benzene was placed on a column of silica gel (55 g.) packed in benzene. Elution with benzene gave 1.60 g. of clear, colorless oil; I.R. (neat) 2960, 1645 (C=N), 1600, 1540 and 1340 (NO$_2$), 1075, 1015, 870, 850, 755 and 700 cm^{-1}, (picrate, m.p. 89-99°), TLC developed in benzene gave a single spot.

Anal. Calcd. for $C_{25}H_{40}N_2O_3$: C, 72.07; H, 9.68; N, 6.73. Found: C, 72.19; H, 9.62; N, 6.66.

(b) From the Hydroxyamide.

9-(4-Nitrobenzamido)-10-hydroxyoctadecane (0.60 g., 0.00138 mole) was heated at 195-200° for 2 hours under a stream of nitrogen. The cooled product, dissolved in hexane, was placed on a column of silica gel (20 g.). Elution with hexane-benzene (1:1) gave a clear, colorless oil (0.42 g., 73.0%) identical in every respect (IR, retention time on GLC and TLC) with 6h isolated under part (a) above.

4,5-Di-*n*-octyl-2-methyl-Δ^2-oxazoline (6a).

9-Acetamido-10-hydroxyoctadecane (0.5 g.) was heated at 220° for 6 hours under nitrogen. The cooled pyrolysate, in hexane, was placed on a Florisil column (25 g.) packed in hexane. Elution with benzene gave pure 6a (0.23 g.) as a colorless oil n_D^{27} = 1.4502; I.R. (neat) 2960, 1670 (C=N), 1385, 1375, 1225, 960 and 825 cm^{-1}. (picrate, m.p. 33.5-35.0°).

Anal. Calcd. for $C_{20}H_{39}NO$: C, 77.61; H, 12.70; N, 4.53. Found: C, 77.82; H, 12.77; N, 4.51.

Comparison of Yields of Hydroxyamides (4) and Δ^2-Oxazolines (6) Obtained from Various Acids.

The addition of carboxylic acids to 2,3-dioctylaziridine was carried out under standardized conditions in order to permit a comparison of the yields of hydroxamides and Δ^2-oxazolines (see Table I). The following procedure is representative and illustrates the method used:

2,3-Dioctylaziridine (1.0 g., 0.0037 mole), benzoic acid (0.57 g., 0.0046 mole) and acetone (4 ml.) were placed in a 10 ml. flask and heated at reflux for 4 hours with stirring. At the end of this period solvent was removed *in vacuo* to give a solid residue (1.57 g.). A portion of the latter (0.80 g.), dissolved in chloroform (25 ml.), was washed with 5% aqueous sodium hydroxide (2 ml.) and water (8 x 3 ml.), was dried over anhydrous sodium sulfate, and was evaporated to a residue (0.76 g.) containing less than 1% 2,3-dioctylaziridine as indicated by TLC (developed with benzene-ether, 9:1). A portion of the residue (0.72 g.) in benzene (15 ml.) was placed on a column of Florisil (30 g., prewashed with benzene, dried, and air-equilibrated overnight) packed in hexane-benzene, 1:1. Elution with hexane-benzene, 1:1 gave 80 mg. of oxazoline 6f. Further elution with benzene-ether, 19:1, gave 500 mg. of

hydroxamide **4f**. The chromatographic procedure was monitored by TLC with use of benzene-ether, 9:1 as the developing solvent.

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